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## Perspective: Maintaining surface-phase purity is key to efficient open air fabricated cuprous oxide solar cells

Robert L. Z. Hoye,<sup>1,a</sup> Riley E. Brandt,<sup>2</sup> Yulia Ilevskaya,<sup>1</sup> Shane Heffernan,<sup>3</sup>  
Kevin P. Musselman,<sup>4,1</sup> Tonio Buonassisi,<sup>2</sup>  
and Judith L. MacManus-Driscoll<sup>1,a</sup>

<sup>1</sup>Department of Materials Science and Metallurgy, University of Cambridge,  
27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom

<sup>2</sup>Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

<sup>3</sup>Electrical Engineering Division, Department of Engineering, University of Cambridge,  
9 JJ Thomson Avenue, Cambridge CB3 0FA, United Kingdom

<sup>4</sup>Department of Physics, University of Cambridge, JJ Thomson Avenue,  
Cambridge CB3 0HE, United Kingdom

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Electrochemically deposited  $\text{Cu}_2\text{O}$  solar cells are receiving growing attention owing to a recent doubling in efficiency. This was enabled by the controlled chemical environment used in depositing doped ZnO layers by atomic layer deposition, which is not well suited to large-scale industrial production. While open air fabrication with atmospheric pressure spatial atomic layer deposition overcomes this limitation, we find that this approach is limited by an inability to remove the detrimental CuO layer that forms on the  $\text{Cu}_2\text{O}$  surface. Herein, we propose strategies for achieving efficiencies in atmospherically processed cells that are equivalent to the high values achieved in vacuum processed cells. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4913442>]

Earth-abundant thin film solar cells, such as  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{ZnSnS}_4$ , are highly promising absorber materials because they are non-toxic and capable of delivering renewable energy on a terawatt level.<sup>1</sup> An important step to enable scalable manufacturing is the fabrication of all components in the cells by low-cost methods.<sup>2</sup> In line with this demand, atmospheric pressure spatial atomic layer deposition (AP-SALD) has evolved from conventional atomic layer deposition (ALD). ALD is a vacuum-based, batch-processed and slow technique, whereas AP-SALD enables the metal oxide deposition to occur rapidly, in open air, at low temperature, and in a roll-to-roll compatible manner, while retaining the high quality of the metal oxides produced by conventional ALD.<sup>3</sup> AP-SALD has proven to be a versatile technique, with the capability of producing ZnO,  $\text{TiO}_2$ , and  $\text{Cu}_2\text{O}$  for high-performing solar cells, in addition to having the ability to introduce dopants into the metal oxides to tune their electronic properties.<sup>3</sup>

While to date only single-digit efficiencies have been demonstrated in all-inorganic  $\text{Cu}_2\text{O}$ -based solar cells,  $\text{Cu}_2\text{O}$  has the strong advantages of compositional simplicity and the use of non-toxic precursor chemicals, which means it has excellent potential for photovoltaic applications, such as use as the top cell in a multijunction device or for water splitting. Recently, the efficiency of electrochemically deposited  $\text{Cu}_2\text{O}$  solar cells has increased from below 2% to reach a certified value of 3.97%.<sup>1,4</sup> These efficiency improvements were mainly due to two factors: reducing the native CuO layer on the surface of the  $\text{Cu}_2\text{O}$  during the deposition of the metal oxide onto the  $\text{Cu}_2\text{O}$  by conventional ALD and reducing the conduction band offset between the *p*-type  $\text{Cu}_2\text{O}$

<sup>a</sup>Authors to whom correspondence should be addressed. Electronic addresses: [rlzh2@cam.ac.uk](mailto:rlzh2@cam.ac.uk) and [jld35@cam.ac.uk](mailto:jld35@cam.ac.uk). Tel.: (44) (0) 1223-334468.



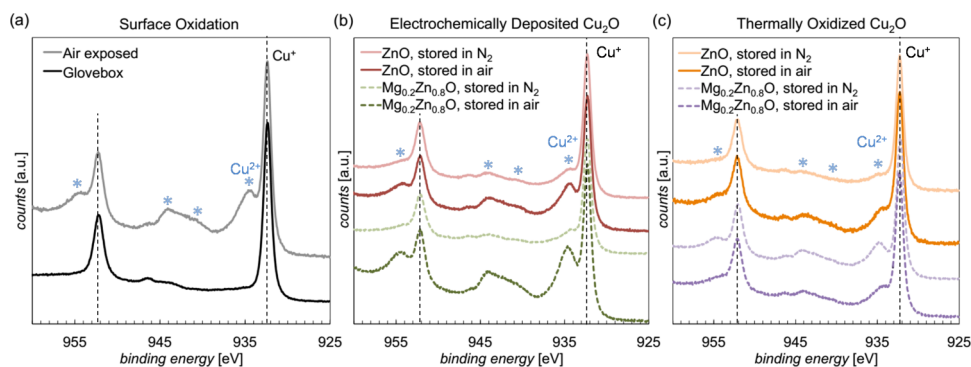


FIG. 1. X-ray photoelectron spectroscopy measurements of Cu-2*p* core levels. (a) Electrochemically deposited Cu<sub>2</sub>O immediately stored in a glovebox vs. stored in air for a week. Comparison of (b) electrochemically deposited and (c) thermally oxidized Cu<sub>2</sub>O with AP-SALD ZnO and Mg<sub>0.2</sub>Zn<sub>0.8</sub>O organometallic precursors scanned over the surface after storage in a glovebox vs. storage in air for a week. The peaks associated with Cu<sup>2+</sup> are indicated by blue asterisks and the peaks associated with Cu<sup>1+</sup> states marked with black dashed lines.

and *n*-type metal oxide.<sup>1,5,6</sup> The presence of surface CuO is detrimental to device performance because its conduction band energy is further from the vacuum level than that of Cu<sub>2</sub>O, and so it produces interfacial defect states that can enhance recombination and reduce photovoltaic device performance.<sup>4,5,7</sup> A similar approach of minimizing both CuO formation, and the conduction band offset was adopted using AP-SALD Zn<sub>1-x</sub>Mg<sub>x</sub>O (where Mg incorporation was used to reduce the conduction band offset),<sup>4,8,9</sup> but the efficiencies obtained could not reach those achieved using ALD ZnO-based materials.<sup>5</sup> Even when Cu<sub>2</sub>O was produced by thermal oxidation, in order to increase the mobility in the absorber, the efficiencies only reached ~2.2%.<sup>4</sup> These were nevertheless the highest obtained for Cu<sub>2</sub>O solar cells with the *p-n* junction fabricated in open air.<sup>4</sup> In this perspective, we investigate the limiting factors for open air fabrication of Cu<sub>2</sub>O-based solar cells and propose strategies for overcoming them. These are important for enabling solar cells with high efficiency absorbers that also face similar surface oxidation limitations, e.g., Cu<sub>2</sub>ZnSnS<sub>4</sub>, to achieve >10% efficiency when fabricated in open air.<sup>10</sup>

We performed X-ray photoelectron spectroscopy (XPS) measurements on electrochemically deposited Cu<sub>2</sub>O films (measurement process detailed in Ref. 6), as shown in Figure 1(a). A Cu<sup>2+</sup> peak (binding energy of 934.2 eV)<sup>5</sup> and satellite peaks at 940–945 eV (Ref. 5) attributed to Cu<sup>2+</sup> were present in the Cu<sub>2</sub>O film left in ambient air for over a week. It was only when the Cu<sub>2</sub>O was stored in a nitrogen-filled glovebox immediately after deposition that peaks associated only with Cu<sup>1+</sup> states were found (Figure 1(a)). It can also be seen from Figures 1(b) and 1(c) that almost all Cu<sub>2</sub>O samples that had been stored in air for a week had higher intensity Cu<sup>2+</sup> peaks than Cu<sub>2</sub>O stored in a nitrogen-filled glovebox for a week. Additional Cu<sup>2+</sup> was introduced because these samples were processed by AP-SALD (details below) at 80 °C (for electrochemically deposited Cu<sub>2</sub>O) or 100 °C (for thermally oxidized Cu<sub>2</sub>O) after storage. These XPS results strongly indicate that CuO readily forms on the Cu<sub>2</sub>O surface when it is exposed to air at room temperature, as indicated by the negative Gibbs free energy in Reaction 1 of Table I. The first technique for minimizing CuO formation is therefore to store the Cu<sub>2</sub>O in an inert environment immediately after deposition.

We investigated whether scanning the Cu<sub>2</sub>O under the flowing vapors of the organometallic precursors for ZnO (diethylzinc) and Mg<sub>0.2</sub>Zn<sub>0.8</sub>O (diethylzinc and bis(ethylcyclopentadienyl) magnesium) from the AP-SALD gas manifold reduced the surface CuO. It has previously been shown that diethylzinc reduces CuO to Cu<sub>2</sub>O in a conventional ALD chamber.<sup>5</sup> However, it could be seen from Figures 1(b) and 1(c) that after organometallic precursor treatment, Cu<sup>2+</sup> peaks remained. This may result from the exposure time of the sample under the organometallic precursors not being long enough to remove the entire CuO layer. Oxygen could also diffuse through the thin (<1 mm) AP-SALD inert gas channels to oxidize Cu<sub>2</sub>O. The difficulty in removing surface CuO may explain the inability of Cu<sub>2</sub>O solar cells formed in open air from reaching the efficiencies achieved by the vacuum production of Cu<sub>2</sub>O solar cells.

TABLE I. Essential reactions that need to be considered when using forming gas to minimize the oxidation of Cu<sub>2</sub>O to CuO, while avoiding the reduction of Cu<sub>2</sub>O or CuO to metallic Cu. All Gibbs free energies are calculated from standard Gibbs formation energies at 298.15 K.<sup>11</sup>

Reaction number	Reaction	$\Delta G_r^0$ (kJ mol <sup>-1</sup> )
1	$\text{Cu}_2\text{O}_{(s)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow 2\text{CuO}_{(s)}$	-113.4
2	$2\text{CuO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Cu}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(g)}$	-115.0
3	$\text{Cu}_2\text{O}_{(s)} + \text{H}_{2(g)} \rightarrow 2\text{Cu}_{(s)} + \text{H}_2\text{O}_{(g)}$	-82.6
4	$\text{CuO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Cu}_{(s)} + \text{H}_2\text{O}_{(g)}$	-98.9

The third technique we consider is introducing reducing H<sub>2</sub> to the inert N<sub>2</sub> gas channels. From Reaction 2 of Table I, it can be seen that the reduction of CuO to Cu<sub>2</sub>O by H<sub>2</sub> gas is thermodynamically favored. But H<sub>2</sub> can also reduce CuO or Cu<sub>2</sub>O to metallic Cu (Reactions 3 and 4 of Table I). The partial pressure of H<sub>2</sub> ( $p_{\text{H}_2}$ ) in the gas mixture and exposure time to the Cu<sub>2</sub>O therefore need to be controlled. We found that thermodynamic considerations are not applicable in the temperature range considered (deposition temperatures of 70–150 °C).<sup>11</sup> By considering the kinetics of the system, CuO formation is minimized when the rate of CuO reduction to Cu<sub>2</sub>O (Reaction 2) is greater than the rate of Cu<sub>2</sub>O oxidation (Reaction 1), as well as being larger than the rates of metallic Cu formation (Reactions 3 and 4). Achieving this balance through H<sub>2</sub> partial pressure control is also dependent on the partial pressure of O<sub>2</sub> that diffuses into the gases under the AP-SALD gas manifold.<sup>11</sup> Previous time-resolved *in-situ* XRD patterns showed that it is possible to maintain Cu<sub>2</sub>O under a flowing mixture of 5% H<sub>2</sub>/95% N<sub>2</sub> without forming metallic Cu at temperatures below 300 °C. These studies also showed that the heating rate is another important parameter to control for the reduction of CuO to Cu<sub>2</sub>O.<sup>12</sup> Thus, the forming gas composition and exposure time to the sample, deposition temperature and heating rate are all parameters that need to be experimentally optimized when minimizing CuO formation by open air AP-SALD processing.

Adopting these three strategies could allow open air fabricated *p-n* junction Cu<sub>2</sub>O solar cells to achieve a similar efficiency as vacuum-processed Cu<sub>2</sub>O solar cells, which can reach 5%.<sup>4</sup> Our strategies are:

- Storing the Cu<sub>2</sub>O in an inert environment immediately after deposition
- Balancing CuO formation with its reduction using forming gas. The forming gas in the AP-SALD gas manifold will prevent Cu<sub>2</sub>O oxidation to CuO. At the same time, limiting H<sub>2</sub> partial pressure and reaction kinetics will prevent the reduction of Cu<sub>2</sub>O to Cu
- Using the organometallic precursors to reduce any remnant surface CuO

In summary, the above strategies should ensure no higher oxidation state species are on the surface of absorber materials prone to surface oxidation, such as Cu<sub>2</sub>O, Cu<sub>2</sub>ZnSnS<sub>4</sub>, CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> and GaAs. This would make AP-SALD a powerful technique for scalably producing efficient (>10%) solar cells.

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